

Forbidden rotational transitions in molecules

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The present state of theoretical and experimental research on forbidden rotational transitions in polar and nonpolar molecules, initiated mainly in 1971, is reviewed. Three mechanisms whereby forbidden rotational transitions appear are considered: 1) centrifugal distortion, 2) anharmonicity of the potential energy, 3) electron-vibrational interaction (the Jahn-Teller effect). A method is described for calculating the effective dipole moment and the strength of a transition, based on successive contact transformations of the Hamiltonian and of the dipole moment operator. Formulas are given for the line strengths of the most important classes of molecules. Results are presented of experimental investigations of centrifugal transitions of tetrahedral hydride molecules by the double resonance and microwave and infrared spectroscopy methods. Particular attention is paid to Jahn-Teller transitions, which have not yet been observed. An approximate estimate is made, for the first time, of the dipole moment of such transitions in triply degenerate electronic states of molecules (such as the ground state of methane) and it is shown that the Jahn-Teller transition strengths can be of the same order as of the anharmonic and centrifugal transitions.

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1. INTRODUCTION

In recent years, owing to the rapid progress in microwave and infrared spectroscopy and to the development of new methods, particularly double-resonance methods, it has become possible to investigate weak spectra of molecules, and primarily forbidden rotational and vibrational-rotational transitions, with intensities lower by several orders of magnitude than those of allowed transitions. Just as in electron spectroscopy of atoms and molecules,^[1,2] the term "forbidden transitions" has no absolute meaning. In our case we have in mind transitions that are forbidden in the adiabatic approximation, in which the interaction between the electronic, vibrational, and rotational motion of the molecule is neglected, and the vibrational-rotational motion of the molecule is described by using the harmonic-oscillator and rigid top models.^[3-7] The results of investigations of forbidden transitions are of interest both from the general physical point of view (determination of the limit of applicability of the adiabatic model, extraction of information on the molecule structure, etc.) and from the practical point of view (identification of the spectra of the interstellar media and planetary atmospheres, elucidation of molecule production and decay mechanisms, and others).

This article deals with three different mechanisms that bring about forbidden dipole rotational transitions of molecules—centrifugal distortion, anharmonicity, and electron-vibrational interaction (the Jahn-Teller effect). The corresponding transitions will henceforth

be called centrifugal, anharmonic, and Jahn-Teller, respectively. Centrifugal transitions can take place in an arbitrary electron-vibrational (vibronic) state of all polar molecules and of a definite class of nonpolar molecules (Chap. 3). Anharmonic and Jahn-Teller transitions appear only in certain degenerate vibronic states (Chap. 5). Since the ground vibronic state of the overwhelming majority of molecules is nondegenerate, centrifugal transitions in the ground states are the only ones possible and most studies are devoted to their experimental study. Anharmonic transitions have been observed only for methane, and no Jahn-Teller transitions have been observed so far.

To make the exposition complete and consistent, we devote Chap. 2 to the calculation of the dipole moment of molecules with allowance for the anharmonicity and vibrational-rotational interaction; the formulas for the strengths of the centrifugal and anharmonic transitions (Chaps. 3 and 4) can be easily derived from the general formulas of Chap. 2. An analogous introduction for Jahn-Teller transitions will be given in Chap. 5.

2. DIPOLE MOMENT OF QUASI-RIGID MOLECULE

The strength of a transition between electron-vibrational-rotational (rovibronic) states i and f is equal to the square of the dipole moment matrix element μ_A referred to a stationary (laboratory) Cartesian coordinate system $A = X, Y, Z^{[1-7]}$:

$$S(i-f) = \sum_{\alpha} \langle i | \mu_{\alpha} | f \rangle^2 \quad (1)$$

If the states i and f are degenerate, then it is necessary to sum in (1) over the degenerate components of i and f . The element μ_{α} can be expressed in terms of the dipole moment components μ_{α} , referred to the axes $\alpha = x, y, z$ of a Cartesian frame rigidly connected with the molecule, using the formula

$$\mu_{\alpha} = \sum_{\alpha} \lambda_{A\alpha} \mu_{\alpha} \quad (2)$$

where $\lambda_{A\alpha}$ are the direction cosines of the stationary axes $A = X, Y, Z$ relative to the moving axes $\alpha = x, y, z$. The matrix elements in (1) should be calculated in the basis of the exact rovibronic eigenfunctions ψ_i and ψ_f of the complete rovibronic Hamiltonian of the molecule, but the latter are unknown. To determine approximate functions we can use the perturbation method. In addition, we assume here (as well as in Chaps. 3 and 4) that the vibrational-rotational motion does not interact with the electronic motion and that the functions ψ_i and ψ_f in (1) pertain only to the vibrational-rotational states and are eigenfunctions of the vibrational-rotational Hamiltonian^[4,8]

$$\mathcal{H} = \sum_{\alpha\beta} (J_{\alpha} - \pi_{\alpha}) B_{\alpha\beta} (J_{\beta} - \pi_{\beta}) + \frac{1}{2} \sum_k \omega_k (p_k^2 + q_k^2) + V_{\alpha} \quad (3)$$

where J_{α} and π_{α} are the components of the total and vibrational angular momenta (dimensionless), $2B_{\alpha\beta}$ is the inverse inertia tensor and depends on the dimensionless normal coordinates q_k , p_k are the momenta conjugate to q_k , ω_k are the vibration frequencies, and V_{α} is the anharmonic part of the potential energy. To apply the perturbation method it is necessary to separate from \mathcal{H} the unperturbed part \mathcal{H}_0 . It is most natural to choose \mathcal{H}_0 in the form of the sum of the Hamiltonians of a rigid top and harmonic oscillators, which is obtained from (1) if we neglect the dependence of $B_{\alpha\beta}$ on q_k and put $V_{\alpha} = 0$ and $\pi_{\alpha} = 0$. Then

$$\mathcal{H}_0 = \frac{1}{2} \sum_k \omega_k (p_k^2 + q_k^2) + \sum_{\alpha} B_{\alpha} J_{\alpha}^2 \quad (4)$$

where B_{α} are the rotational constant of the rigid molecule. The eigenfunctions ψ_0 of the operator \mathcal{H}_0 are products of eigenfunctions ψ_R of the rigid top by the eigenfunctions ψ_V of the harmonic oscillators

$$\psi_0 = \psi_R \psi_V = \psi_R \psi_{V_1} \psi_{V_2} \dots \psi_{V_n} \quad (5)$$

In the ψ_0 basis, the dipole-moment matrix elements are

$$\langle VR | \mu_{\alpha} | V'R' \rangle = \sum_{\alpha} \langle V | \mu_{\alpha} | V' \rangle \langle R | \lambda_{A\alpha} | R' \rangle \quad (6)$$

and if μ_{α} is independent of q_k then

$$\langle V | \mu_{\alpha} | V' \rangle = \mu_{\alpha}^e \delta_{VV'} \quad (7)$$

but since $\mu_{\alpha}^e = 0$ for nonpolar molecules, the rotational spectrum of such molecules is forbidden. For polar molecules of the symmetric-top type ($\mu_x^e \neq 0$, $\mu_x^e = \mu_y^e = 0$) the only transitions allowed in this approximation are

those with $\Delta J = 0, \pm 1$, $\Delta K = 0$ (K is the quantum number of the projection of the total angular momentum on the symmetry axis). Thus, in the approximation of the harmonic oscillator and rigid top, the nonpolar molecules have no rotational spectrum, while the rotational spectra of polar molecules are limited by the selection rule $\Delta K = 0$.^[3-7] We shall show now that if we start not from (5) but from the complete Hamiltonian (3), then this rule is essentially different.

For convenience, we expand \mathcal{H} in powers of q_k and denote the individual terms of the series by^[9] \mathcal{H}_{nm} , where n is the degree of the polynomial in q_k and p_k , while m is the degree of the polynomial in J_{α} . In the first approximation (following Nielsen^[10]) we then obtain

$$\mathcal{H} = \mathcal{H}_{20} + \mathcal{H}_{02} + \mathcal{H}_{12} + \mathcal{H}_{30} + \mathcal{H}_{21} \quad (8)$$

where the expression $\mathcal{H}_{20} + \mathcal{H}_{02}$ is given in (5), and the remaining terms are equal to

$$\mathcal{H}_{12} = \sum_{\alpha\beta} B_{\alpha\beta}^{\alpha\beta} q_{\alpha} J_{\beta}, \quad B_{\alpha\beta}^{\alpha\beta} = \left(\frac{\partial B_{\alpha\beta}}{\partial q_{\alpha}} \right)_e \quad (9)$$

$$\mathcal{H}_{30} = \frac{1}{6} \sum_{ijk} K_{ijk} q_i q_j q_k, \quad K_{ijk} = \left(\frac{\partial^3 V_{\alpha}}{\partial q_i \partial q_j \partial q_k} \right)_e \quad (10)$$

$$\mathcal{H}_{21} = -2 \sum_{jk} \sqrt{\frac{\omega_j}{\omega_k}} q_k p_j \sum_{\alpha} B_{\alpha} \zeta_{kj}^{\alpha} J_{\alpha} \quad (11)$$

where ζ_{kj}^{α} are the Coriolis-interaction constants. The expansion of μ_{α} can be expressed in the form

$$\mu_{\alpha} = \mu_{00}^{\alpha} + \mu_{10}^{\alpha} + \mu_{20}^{\alpha} + \dots \quad (12)$$

where

$$\begin{aligned} \mu_{00}^{\alpha} &= \mu_{\alpha}^e, \quad \mu_{10}^{\alpha} = \sum_k \left(\frac{\partial \mu_{\alpha}}{\partial q_k} \right)_e q_k, \\ \mu_{20}^{\alpha} &= \frac{1}{2} \sum_{jk} \left(\frac{\partial^2 \mu_{\alpha}}{\partial q_j \partial q_k} \right)_e q_j q_k. \end{aligned} \quad (13)$$

Transitions that are allowed on account of \mathcal{H}_{12} (with μ_{10} and μ_{00}) will be called centrifugal, since \mathcal{H}_{12} describes the distortion of the molecule by the rotation, while the transitions allowed on account of \mathcal{H}_{30} (with μ_{10} and μ_{20}) will be called anharmonic. In first-order approximation, \mathcal{H}_{21} does not lead to violation of the selection rules for the purely rotational transitions.

To calculate μ_{α} in accordance with the model (8) we can use the contact-transformation method,^[9,10] the gist of which is the following: The unitary transformation $\exp(iS)$ reduces the operator \mathcal{H} to the form

$$\begin{aligned} \tilde{\mathcal{H}} &= \exp(iS) \mathcal{H} \exp(-iS) \\ &= \mathcal{H} + i[S, \mathcal{H}] - \frac{1}{2}[S, [S, \mathcal{H}]] + \dots ([S, \mathcal{H}] = S\mathcal{H} - \mathcal{H}S), \end{aligned} \quad (14)$$

which is diagonal in the ψ_0 basis. The calculation of $\langle i | \mu_{\alpha} | l \rangle$ in the ψ basis then reduces to a calculation of the matrix elements of the operator

$$\tilde{\mu}_{\alpha} = \exp(iS) \mu_{\alpha} \exp(-iS) = \mu_{\alpha} + i[S, \mu_{\alpha}] - \frac{1}{2}[S, [S, \mu_{\alpha}]] + \dots \quad (15)$$

in the ψ_0 basis. In our case we need to transform \mathcal{H} (and μ_{α}) twice. The first transformation with the generator^[9]

$$S = S_{30} + S_{12} + S_{21} \quad (16)$$

diagonalizes $\mathcal{H}_{30} + \mathcal{H}_{12} + \mathcal{H}_{21}$ with respect to the vibrational quantum numbers if

$$S_{30} = -\frac{1}{6} \sum_{ijk} K_{ijk} \Omega_{ijk}^2 [2\omega_i \omega_j \omega_k p_i p_j p_k + 3\omega_k (\omega_i^2 + \omega_j^2 - \omega_k^2) q_i p_k q_j], \quad (17)$$

$$S_{21} = \frac{1}{2} \left[\sum_{ij} R_j^i (\omega_i + \omega_j)^{-1} (q_i q_j - p_i p_j) + \sum_{ij}^* R_j^i (\omega_i - \omega_j) (q_i q_j + p_i p_j) \right], \quad (18)$$

$$S_{12} = - \sum_k \sum_{\alpha\beta} \frac{B_k^{\alpha\beta}}{\omega_k} p_k J_\alpha J_\beta, \quad (19)$$

where

$$\Omega_{ijk} = (\omega_i + \omega_j + \omega_k) (-\omega_i + \omega_j + \omega_k) (\omega_i - \omega_j + \omega_k) (\omega_i + \omega_j + \omega_k), \\ R_i^j = -(\omega_j/\omega_i) R_j^i = -2 \sqrt{\frac{\omega_l}{\omega_i}} \sum_\alpha B_{\alpha} \zeta_{ij}^\alpha J_\alpha.$$

Substitution of (8)–(11) and (17)–(19) in (14) yields the effective Hamiltonian \mathcal{H} . We shall need subsequently only a part of \mathcal{H} , equal to¹⁾

$$\mathcal{H}_R = \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \tau_{\alpha\beta\gamma\delta} J_\alpha J_\beta J_\gamma J_\delta, \quad (20)$$

where

$$\tau_{\alpha\beta\gamma\delta} = -2 \sum_k \frac{B_k^{\alpha\beta} B_k^{\gamma\delta}}{\omega_k} \quad (21)$$

are called the constants of the quadratic centrifugal distortion of the molecules. \mathcal{H}_R does not commute with \mathcal{H}_{02} . By a second transformation, however, it can be reduced to the form $\mathcal{H}_R = \exp(iS_R) \mathcal{H}_R \exp(-iS_R)$ which commutes with \mathcal{H}_{02} .^[11] The explicit form of S_R will be given in Chap. 3.

As a result of the two transformations we obtain for μ_A

$$\tilde{\mu}_A = \sum_\alpha \lambda_{A\alpha} \mu_\alpha^e + i \sum_\alpha ([S_{12}, \mu_\alpha^e] \lambda_{A\alpha} + [S_R, \lambda_{A\alpha}] \mu_\alpha^e) \\ + \sum_\alpha \lambda_{A\alpha} (\mu_{20}^\alpha + i [S_{30}, \mu_\alpha^e]) + \dots \quad (22)$$

The first term in (22) corresponds to the purely rotational spectrum of a rigid polar molecule,^[5-7] while the second corresponds to forbidden transitions (with $\Delta K \leq 4$), which become allowed by the centrifugal distortion (see Chap. 3), while the third term corresponds to forbidden transitions (with $\Delta K \leq 1$) which are allowed on account of the mechanical ($[S_{30}, \mu_\alpha^e]$) and electro-optical anharmonicity (see Chap. 4). If we include the next higher terms in the series (8), then new terms, corresponding to transitions with $\Delta K > 4$, will appear in the expansion (22). Thus, allowance for the vibrational-rotational interaction and for the anharmonicity alters qualitatively the spectra of the molecules—a new forbidden spectrum appears for a nonpolar molecules and new transitions in the spectra of polar molecules.

¹⁾We note that formula (20) can be obtained also by combining \mathcal{H}_{12} with \mathcal{H}_{20} (coordinate shift). However, since \mathcal{H}_{12} does not commute with \mathcal{H}_{02} , this method can be used in the approximations of higher order.

3. CENTRIFUGAL TRANSITIONS^[12-17]

In this section we shall dwell on the conditions for the appearance of rotational transitions on account of the centrifugal part $\tilde{\mu}_A$ in (22). We consider for convenience polar molecules ($\mu_\alpha^e \neq 0$) of the symmetric-top type ($B_x = B_y \neq B_z$) and nonpolar molecules ($\mu_\alpha^e = 0$) of the symmetric and spherical ($B_x = B_y = B_z$) top type separately. Inasmuch as in molecules of the asymmetric top ($B_x \neq B_y \neq B_z$) type transitions with $\Delta K > 0$ are allowed even in the zeroth approximation, we shall not consider them here, although the general formulas for polar symmetrical tops are valid also for asymmetrical tops.²⁾

A. Nonpolar molecules

In this case $\mu_\alpha^e = 0$ and the second term of (22) takes the form

$$\mu_A^{\text{cent}} = i \sum_\alpha [S_{12}, \mu_\alpha^e] \lambda_{A\alpha}, \quad (23)$$

and, if (13) and (18) are taken into account,

$$\mu_A^{\text{cent}} = \frac{1}{2} \sum_{\alpha\beta\gamma} \Theta_\alpha^{\beta\gamma} (\lambda_{A\alpha} J_\beta J_\gamma + J_\gamma J_\beta \lambda_{A\alpha}), \quad (24)$$

where the aggregate of the quantities

$$\Theta_\alpha^{\beta\gamma} = \Theta_\alpha^{\gamma\beta} = \sum_k \frac{B_k^{\beta\gamma}}{\omega_k} \frac{\partial \mu_\alpha}{\partial q_k} \quad (25)$$

has been named the centrifugal dipole moment. Consequently, in order for a nonpolar molecules to have a rotational spectrum, at least one of the components of the tensor $\Theta_\alpha^{\beta\gamma}$ must differ from zero, and to this end the molecule must have at least one normal coordinate along which the derivatives of the dipole moment and of the inertia tensor are nonzero. It has been shown^[12, 14] that this condition is satisfied only for molecules belonging to the point groups D_n , D_{2d} , D_{3h} , C_{3h} , T_d , T , and S_4 . The transition strengths can be obtained with allowance for the symmetry properties of the tensor $\Theta_\alpha^{\beta\gamma}$ in (24) after substituting (24) in (1) and calculating the matrix elements $\lambda_{A\alpha}$ and J_α in the basis of the wave functions of the rigid symmetric top.^[5-7]

The most complete experimental investigations of forbidden transitions, which confirm the centrifugal mechanism, were performed in recent years for tetrahedral hydrides. We shall therefore dwell in greater detail on this class of molecules. In the zeroth approximation the rotational wave functions of the vibronic ground state can be classified in terms of the irreducible representations $D^{(J)}$ of the group of three-dimensional rotations, a level with given value $2J+1$ of J is multiply degenerate in the quantum number K . When the centrifugal distortion is taken into account^[19-21] the order of the symmetry group of the Hamiltonian is lowered and the degeneracy in K is partly lifted. Then the rotational energy of a tetrahedral molecule in the ground state can then

²⁾Centrifugal transitions in forbidden Raman spectra of tetrahedral molecules were considered by Verlain.^[18]

Molecule	Transition	Frequency range	Absorption coefficient	Molecular constants*	Reference
CH ₄	Ortho-para J=2	10-30 kHz in field 2000 G	-	$\mu_D = (5.38 \pm 0.10) \cdot 10^{-4}$ Debye	25
	Q-branch J=2-18	7-20 GHz	(2-6) $\times 10^{-11}$ cm ⁻¹	$D_t = 132943.41 \pm 0.71$ Hz, $H_{4t} = -(16.9839 \pm 0.0076)$ Hz, $H_{6t} = 11.0342 \pm 0.0086$ Hz	29
	Q-branch, J=7	0.4-1.3 GHz	-	$D_t = 132.93$ kHz, $H_{4t} = -16.6$ Hz, $H_{6t} = 10.2$ Hz	28
SiH ₄	R-branch, J → J+1 = 7 → 8 - 16 → 17	80-200 cm ⁻¹	$\leq 0.5 \cdot 10^{-3}$ cm ⁻¹	$B_0 = 5.245$ cm ⁻¹ , $D_J = 1.19 \cdot 10^{-4}$ cm ⁻¹	22, 30
	Q-branch J=5 and 9	Near 0.1 and 1 GHz	10^{-12} - 10^{-17} cm ⁻¹	$D_t = 74861 + 15$ Hz, $H_{4t} = -7.14 \pm 0.3$ Hz, $H_{6t} = 6.57 \pm 1.1$ Hz,	23b
	R-branch J → J+1 = 10 → 11 - 22 → 23	60-135 cm ⁻¹	$\leq 0.75 \cdot 10^{-3}$ cm ⁻¹	$B_0 = 2.8574 + 0.0027$ cm ⁻¹ , $D_J = (3.48 + 0.54) \cdot 10^{-5}$ cm ⁻¹ , $\mu_D = 8.3 \cdot 10^{-6}$ Debye	23
GeH ₄	R-branch, J → J+1 = 9 → 10 - 23 → 24	50-130 cm ⁻¹	$\leq 0.7 \cdot 10^{-3}$ cm ⁻¹	$B_0 = 2.696 \pm 0.003$ cm ⁻¹ , $D_J = (3.3 \pm 0.6) \cdot 10^{-5}$ cm ⁻¹ , $\mu_D = 7.7 \cdot 10^{-6}$ Debye	24

*) $\mu_D = \theta_{\text{eff}}^{\text{av}} / \sqrt{20}$.

be expressed in the form^[21]

$$E = BJ(J+1) - D_J J^2(J+1)^2 + H_J J^3(J+1)^3 + [D_t + H_{4t}(J+1)]f(J, k) + H_{6t}g(J, k), \quad (26)$$

where B is the rotational constant and D_J and H_J are the constants of the quartic and sextic scalar centrifugal distortion, which causes no level splitting, while D_t , H_{4t} , and H_{6t} are the constants of the quartic (D) and sextic (H) tensor centrifugal distortion, which does cause level splitting.^[19-21] D_J and D_t depend only on the harmonic strength constants, while H_J and H_{4t} , H_{6t} also on the cubic anharmonicity coefficients. Formulas connecting D and H with the molecular parameters are given in^[9]. The splitting of a level with a given value of J , due to the tensor terms in (7), has been called "tetrahedral" splitting. The functions $f(J, k)$ and $g(J, k)$ are tabulated in^[21]. The rotational spectrum consists of the branches $R(J \rightarrow J+1)$ and $Q(J \rightarrow J)$, with the frequencies of the R -branch lines determined by the value of B , while the frequencies of the Q branch are determined by the value of D_t ($D_t \gg H_{4t}$, H_{6t}): for hydrides, the R branch falls in the long-wave infrared region and the Q branch in the microwave and radio-frequency regions of the spectrum. The Q -branch line strengths can be determined only numerically, and the integrated strength of J multiplet of the R branch ($J \rightarrow J+1$) is given by^[12,13,16]

$$S(J \rightarrow J+1) = \frac{2}{35} (\theta_{\text{eff}}^{\text{av}})^2 J(J+1)(2J-1)(2J+1)(2J+3)(2J+5). \quad (27)$$

The R branch with unresolved tetrahedral structure of

the molecule CH₄ ($9 \leq J \leq 16$) was first observed in the 100-180 cm⁻¹ region by Rosenberg, Ozier, and Kudian,^[22] who used a Michelson interferometer and a multiple-pass cell with optical path length 139 m, at pressures 0.75-1.6 atm and at room temperature. This was followed by detailed investigations of the R branch and by a determination of the rotational constants and the dipole moments of the molecules SiH₄^[23] and GeH₄.^[24] The first confirmation of the existence of a centrifugal dipole moment, however, was obtained, however, earlier by Ozier^[25] in an investigation of ortho-para transitions in CH₄ by the level-crossing method.^[26]

A detailed calculation of the frequencies, intensities, and the Stark effect for the CH₄ Q -branch lines was carried out by Dorney and Watson^[16] and by Fox.^[13] The results of these calculations have stimulated unusual experiments performed by Oka and co-workers^[27,28] and by Ozier and co-workers.^[29] In^[27,28] infrared radio-frequency double resonance and an He-Ne laser were used to identify the lines of the transitions between the tetrahedral components of the rotational levels of the vibrational ground state of methane. Ozier *et al.*^[21] have observed four Q -branch absorption lines, with an absorption coefficient $\sim 5 \cdot 10^{-10}$ cm⁻¹, using a Stark spectrometer and a registration system with storage. The results of these measurements are listed in the table.

The most abundant molecules of the class of nonpolar molecules of the symmetric-top type, having a dipole centrifugal spectrum are those with symmetry D_{3h} (BF₃,

C_3H_6 , etc). The line strengths for the transitions $K \rightarrow K + 3$ of the R branch ($J \rightarrow J + 1$) of these molecules are determined by the expression^[12, 15]

$$S(J \rightarrow J + 1, K \rightarrow K + 3) = (1/4)(\Theta_x^{\alpha x})^2 (J + K + 1)(J + K + 2)(J + K + 3)(J + K + 4) \times (J - K)(J - K - 1)(J + 1)^{-1}, \quad (28)$$

and for the transitions $J \rightarrow J$ and $K \rightarrow K + 3$ (Q branch) we have

$$S(J \rightarrow J, K \rightarrow K + 3) = (1/4)(\Theta_x^{\alpha x})^2 (J - K)(J - K - 1)(J - K - 2)(J + K + 1) \times (J + K + 2)(J + K + 3)(2J + 1)[J(J + 1)]^{-1}. \quad (29)$$

The line strengths for the remaining classes of molecules are tabulated in^[15]. It is seen from these formulas that the strengths of the forbidden transitions depend on J^5 , whereas the strengths of the allowed perpendicular transitions^[2] with $\Delta K = \pm 1$ depend on J^1 . Therefore at large J the intensities of the forbidden transitions, for quasi-polar molecules with $\mu \sim 0.01$ Debye, are comparable with the intensities of the allowed transitions.^[17]

Forbidden transitions in polar molecules of the symmetric-top type have not yet been observed. Estimates,^[12, 15] however, point to the feasibility of observing these transitions by existing methods that permit registration of lines with peak absorption coefficients $\alpha_m \sim 6 \times 10^{-13} \text{ cm}^{-1}$ in the microwave band^[31] and $\alpha_m \sim 10^{-9} \text{ cm}^{-1}$ in the submillimeter band.^[32]

As shown by Watson,^[33] the first-order Stark effect exists for all nonpolar molecules, with the exception of the E states of tetrahedral molecules. The presence of quasi-degeneracies such as l and K splitting likewise does not contribute to the onset of a first-order Stark effect. Furthermore, since the second-order Stark effect decreases^[5-7] with increasing J , the quadratic dependence of the centrifugal dipole moment on J cannot produce a discernible Stark effect needed for the realization of the standard Stark-modulation method. To measure forbidden spectra of nonpolar molecules (especially of the symmetric-top type) new methods are therefore needed, primarily double-resonance methods.

B. Polar molecules

For polar molecules of the centrifugal-top type $\mu_x^e \neq 0$ and the centrifugal dipole moment is determined from the formula^[17]

$$\bar{\mu}_A^{\text{cent}} = i \sum_{\alpha} \{ [S_{12}, \mu_{10}^{\alpha}] \lambda_{A\alpha} + [S_R, \lambda_{A\alpha}] \mu_{\alpha}^e \}, \quad (30)$$

which can also be rewritten in the form (24) with new parameters

$$\bar{\Theta}_{\alpha}^{\beta\gamma} = \Theta_{\alpha}^{\beta\gamma} + \Theta_{\alpha}^{\beta\gamma}(R), \quad (31)$$

where $\Theta_{\alpha}^{\beta\gamma}$ is given by (25), and to determine $\Theta_{\alpha}^{\beta\gamma}(R)$, which is the result of the second term in (30), we must know the rotational transformation operator S_R that diagonalizes the rotational Hamiltonian \mathcal{H}'_R of (20).^[11] From the symmetry properties of the parameters Θ it

follows that in the class of polar symmetrical tops the only nonzero $\bar{\Theta}_{\alpha}^{\beta\gamma}$ are possessed by molecules of symmetry C_n and C_m with $n = 3$ and 4 , wherein for the molecules of symmetry C_3 and C_{3v} both terms of (31) differ from zero, while for molecules of symmetry C_4 and C_{4v} the first term of (31) vanishes.^[17] For molecules of symmetry C_{3v} , the off-diagonal part of the rotational Hamiltonian is equal to^[11]

$$\mathcal{H}'_R(C_{3v}) = \frac{\tau_{xxzz}}{4} \{ ([J_x^2 - J_y^2], [J_x, J_z]_+ - [J_y, J_z]_+) + [J_x, J_y]_+ \}, \quad (32)$$

where $[A, B]_{\pm} = AB + BA$, and the operator S_R which diagonalizes $\mathcal{H}'_R(C_{3v})$ is^[11]

$$S_R = \frac{\tau_{xxzz}}{4(B_x - B_z)} \left([J_x^2, J_y]_+ - \frac{2}{3} J_y^2 - \frac{1}{3} J_y \right). \quad (33)$$

We note that the diagonal elements $\mathcal{H}'_R(C_{3v})$ are equal to zero, and the off-diagonal elements with $\Delta K = \pm 3$ split, in the second-order approximation, the rotational levels with $|K| = 3$ of the nondegenerate vibrational states.^[9]

For molecules of C_{4v} symmetry, the rotational-Hamiltonian component that contributes to μ_A^{cent} is of the form^[17]

$$\mathcal{H}'_R(C_{4v}) = \frac{\tau_{xyxy}}{4} [J_x, J_y]_+^2 - \frac{\tau_{xxzz}}{4} (J_x^2 - J_y^2)^2. \quad (34)$$

The nonzero matrix elements of the operator S_R are determined in this case by the formula

$$\langle K | S_R | K \pm 4 \rangle = \frac{i(K | H' | K \pm 4)}{E_{K \pm 4} - E_K}. \quad (35)$$

Then, using (formulas (30), (33), (35), and (1), we obtain for the transition strengths^[17]

$$S(J \rightarrow J', K \rightarrow K') = [\bar{\Theta}(G)]^2 F(J \rightarrow J', K \rightarrow K'), \quad (36)$$

where

$$\bar{\Theta}(C_{3v}) = \bar{\Theta}_x^{\alpha x} + \frac{\mu_x^e \tau_{xxzz}}{2(B_x - B_z)}, \quad (37)$$

$$\bar{\Theta}(C_{4v}) = \frac{\mu_x^e (\tau_{xxzz} B_z + \tau_{xyxy})}{4(B_z - B_x)}, \quad (38)$$

and the expressions for $F(J \rightarrow J', K \rightarrow K')$ are tabulated in^[17].

Thus, the main difference between the centrifugal transitions in polar molecules and the centrifugal transitions in nonpolar molecules is that the transitions with $\Delta K > 0$ ($\Delta K = \pm 3$ for C_{3v} and $\Delta K = \pm 4$ for C_{4v}) in polar molecules are allowed not only because of the mixing of the rotational wave functions of the ground and excited vibrational levels, due to the first term in (30) (as in the case of nonpolar molecules), but also to the mixing of the rotational wave functions of the same vibrational state.

Centrifugal transitions with $\Delta K = \pm 3$ have been observed in the rotational spectra of the molecules NH_3^{34} , PH_3^{35} and AsH_3^{36} . Transitions with $\Delta K = \pm 3$ were identified also in the infrared vibrational-rotational spectra of the molecules CH_3D^{37} , PH_3^{38} and AsH_3^{39} . As a result, a complete set of vibrational-rotational constants was obtained for these molecules, including also such

constants (A_0 , D_K , H_K and others) the values of which can not be determined from the frequencies of the allowed transitions. It should be noted that the values of the sextic centrifugal constants obtained in these studies can be used for the solution of the anharmonic problem.^[9, 40]

4. ANHARMONIC ROTATIONAL TRANSITIONS IN DEGENERATE VIBRATIONAL STATES

The centrifugal mechanism considered above contributes to the lifting of the hindrance from the rotational transitions not only in the ground state but also in the excited degenerate vibrational states. In some excited degenerate vibrational states, however, the lifting of the hindrance may be connected with the third term in (22) (the anharmonicity of the potential energy and the nonlinearity of the dipole moment),^[41, 42] and for low rotational states the intensities of these transitions are higher by 2–6 orders of magnitude than the intensities of the centrifugal transitions. In the region of the maximum of the rotational band, the intensities of the centrifugal and harmonic transitions can be comparable. Since the selection rules for these two types of transitions are entirely different, their identification entails no difficulty. In this section we consider briefly the results of the investigation of anharmonic transitions due to the third term in (22); after subtracting the commutator [S_{30} , μ_{10}^α], this term takes the form

$$\mu_{10}^{\text{ang}} = \sum_{\alpha} \lambda_{A\alpha} \sum_{j,k} \left\{ \frac{1}{2} \frac{\partial^2 \mu_{\alpha}}{\partial q_j \partial q_k} q_j q_k - \sum_i \frac{K_{ijk} \omega_i}{\Omega_{ijk}} \frac{\partial \mu_{\alpha}}{\partial q_i} \left[\omega_j \omega_k p_j p_k + \frac{1}{2} (\omega_j^2 + \omega_k^2 - \omega_i^2) q_j q_k \right] \right\}. \quad (39)$$

For simplicity, it is convenient to subdivide the molecules with anharmonic transitions into three groups^[41]: 1) molecules with a rotary symmetry axis C_n , 2) molecules with a mirror symmetry axis S_n , and 3) tetrahedral molecules. In molecules having a symmetry center and in linear molecules, the anharmonicity, as well as the centrifugal distortion, does not lift the hindrance. The symmetry conditions for the dipole-moment matrix element show that a molecule from the first group can have a spectrum only in a doubly degenerate state such as the symmetry $E_{(n-1)/2}$, if the symmetry C_n has odd multiplicity (n is odd), with the allowed transitions polarized along the axes x and y which are perpendicular to the C_n axis, and satisfying the selection rules $\Delta J = 0, \pm 1$, $\Delta K = \pm 1$ and $\mp l \rightarrow \pm l$, where l is the quantum number of the vibrational angular momentum. The anharmonic spectrum has therefore the same structure as the "perpendicular" vibrational-rotational band. The vibrational factor of the dipole-moment matrix element for these transitions in a state with $|l| = 1$, after taking into account the symmetry relations between the parameter and substituting the matrix elements q_j and p_j in (39), can be written in the form^[41]

$$\mu_t = \frac{\partial^2 \mu_x}{\partial q_x^2} - \sum_{t'} \frac{K_{t_x t' t'_x}}{\omega_{t'}} \frac{\partial \mu_x}{\partial q_{t'_x}}, \quad (39a)$$

where t and t' are the numbers of the degenerate oscillations. The rotational factor of the line strengths is

identical with the Henle-London factor.^[43] A reliable estimate of the values of μ_t is made difficult in (39a) because of the lack of data on the parameters $\partial^2 \mu / \partial q^2$ and the anharmonicity coefficients $K_{t_x t' t'_x}$, and estimates for simple molecules such as ethane, alene, BCl_3 etc. yield in the two-atom approximation $\mu_3 \sim 10^{-3} - 10^{-4}$ D. Consequently, if we disregard the Boltzmann factor, the absorption coefficients of the anharmonic transitions are smaller by 4–8 orders than those of ordinary rotational spectra of polar molecules with dipole moment ~ 1 D.

In molecules with rotation symmetry axis S_n with odd n , the anharmonic rotational transitions polarized perpendicular to the S_n axis are allowed also in states of the type $E_{(n-1)/2}$, the structure of the spectrum is exactly the same as for molecules with C_n axis, and the dipole moment is determined by (39a). In molecules with S_n axis having $n = 4s$, however, transitions parallel to the S_n axis (z transitions) are also possible in states of type E_s , and these transitions satisfy the selection rules $\Delta J = 0, \pm 1$, $\Delta K = 0, -l \rightarrow +l$. They form two series of Q branches with frequencies $\pm 4B_x \zeta_i^2 K$ (ζ_i^2 is the Coriolis-interaction constant) and corresponding R and P branches.^[41] Formula (39), after division by 2 and replacement of x and t' by z and s (s is the number of the oscillations of B_2 type) respectively is valid also for parallel transitions.

For molecules of the spherical top type (point groups T_d and T), anharmonic rotational transitions are allowed only in vibrational states of symmetry $F(T)$ or F_1 and $F_2(T_d)$. The vibrational factor of the dipole-moment matrix element is

$$\mu_t = \frac{1}{2} \left(\frac{\partial^2 \mu_z}{\partial q_x \partial q_y} - \sum_{t'} \frac{K_{t_x t' t'_z}}{\omega_{t'}} \frac{\partial \mu_z}{\partial q_{t'_z}} \right). \quad (40)$$

The dipole moment of the state ν_3 of the CH_4 molecule was measured several times by laser spectroscopy methods, and is equal to $\mu_3 = 0.0204$ D.^[43–45] It must be noted that for heavier molecules (CF_4 , CCl_4 , SiF_4 , etc.) the moment should be of the order of $\sim 10^{-2} - 10^{-4}$ D^[46] and observation of the rotational spectra of such molecules in excited states is feasible, in view of their relatively large population, by available microwave spectroscopy methods.^[25, 29, 31, 32] The peak absorption coefficients of the lines of such molecules, as well as of molecules of the BCl_3 type in the millimeter and submillimeter bands amount to $10^{-6} - 10^{-10} \text{ cm}^{-1}$, while the limiting sensitivity of the optical-acoustic registration method, reached by Krupnov *et al.*,^[32] is 10^{-9} cm^{-1} . In the centimeter band where the attained sensitivity limit is 10^{-13} cm^{-1} ,^[31] the absorption coefficients of the lines of the molecules in question amount to $10^{-10} - 10^{-14} \text{ cm}^{-1}$, reaching values $10^{-3} - 10^{-6} \text{ cm}^{-1}$ in the long-wave infrared region of the spectrum ($30 - 100 \text{ cm}^{-1}$). For the quasi-polar molecules CH_3CD_3 and $\text{C}_3\text{H}_2\text{D}_2$, whose dipole moments are 0.01078 and 0.00031 (i.e., close to the dipole moments of nonpolar molecules), microwave rotational transitions have already been observed.^[47] The rotational spectrum of the molecule CH_3D ($\mu_x^0 = 5.68 \times 10^{-3}$ D) in the region $40 - 120 \text{ cm}^{-1}$ was also measured.^[48]

In excited degenerate vibrational states higher than the first, peculiar microwave vibrational-rotational spectra can appear. For example, the doubly excited state of the doubly degenerate vibration of a molecule with C_{3v} symmetry is split by anharmonicity into components with $l=0$ and 2. Transitions between rotational levels with $l=0$ and 2 make up a band of the perpendicular type,^[49] the position of the center of which depends on the anharmonicity constants $4x_{11}$. For hydrides ($x_{11} \sim 10-100 \text{ cm}^{-1}$) this band can be encountered in the long-wave infrared, while for heavy molecules ($x_{11} \sim 1-10 \text{ cm}^{-1}$) this band lies in the microwave region.

Anharmonicity of the potential energy and nonlinearity of the dipole moment can thus cause nonpolar molecules in certain degenerate vibrational states to have a rotational spectrum. The presence of this spectrum is determined from the symmetry condition, according to which, in order for a spectrum to appear in a state with symmetry type Γ , the symmetric product $[\Gamma^2]$ must contain the symmetry type $\Gamma(\mu_\alpha)$ of one of the dipole-moment components. Since the intensity of the anharmonic transitions depends on the cubic anharmonicity coefficients and on the second derivatives of the dipole moment, the experimental data on the intensity of the anharmonic spectra, alongside the intensity of the vibrational overtones, can be used to determine the functions of the dipole moment and of the potential energy of the molecules.

5. JAHN-TELLER ROTATIONAL TRANSITIONS IN DEGENERATE ELECTRONIC STATES

Molecules in degenerate electronic states can have, besides centrifugal and anharmonic spectrum, also a rotational spectrum due to the Jahn-Teller coupling^[50] between the electronic and vibrational motions. The first to indicate this possibility were Child and Longuet-Higgins^[51] with molecules of D_{3h} symmetry as examples. Bersuker, Ogurtsov, and Shparev^[52] have recently considered the tunnel-rotational spectrum of tetrahedral molecules in the case of the static Jahn-Teller effect. Since these spectra have not yet been observed experimentally, it is of interest to consider the mechanism whereby they are produced and to assess the feasibility of observing these spectra.

As shown by Jahn and Teller,^[50] an orbitally degenerate electronic state of a nonlinear molecule is unstable to certain not-fully-symmetrical displacements of the nuclei. Therefore a configuration of nuclei with highest symmetry is not the equilibrium configuration corresponding to the minimum potential energy. Vibronic states can split, and the potential-energy surface can have several minima. This does not mean, however, that the symmetry of the vibronic Hamiltonian is lowered. The Hamiltonian is in all cases invariant to the Longuet-Higgins group of permutations-inversions,^[53] just as in the case of non-rigid molecules. The Jahn-Teller effect causes a lowering of the symmetry of the geometric configurations, and hence of the distribution of the electron density, relative to the maximum possible geometric symmetry, which cannot be higher than the permutation-inversion symmetry,^[53] since the ge-

ometric point groups are always subgroups of the corresponding permutation-inversion groups. The onset of a dipole moment and of a rotational spectrum in a degenerate electronic state of a "nonpolar molecule" is due precisely to the lowering of the symmetry of the electron-density distribution relative to the symmetry of the nonpolar geometric configuration, as a result of the Jahn-Teller effect.

The symmetry selection rules for Jahn-Teller transitions are analogous to the selection rules for anharmonic (but not centrifugal) transitions given in Sec. 3. In particular, for tetrahedral molecules, to which we confine ourselves here, the Jahn-Teller transitions can appear only in triply degenerate electronic states of the type F_1 and F_2 , for only $[F_1^2]$ and $[F_2^2]$ contain the symmetry type F_2 of the dipole moment.

Let us consider the most important class of molecules AB_4 of symmetry T_d in an electronic state of type F_1 or F_2 , and write down the vibronic Hamiltonian in the form^[54-59]

$$\mathcal{H} = V \sum_{\alpha} q_{\alpha} T_{\alpha} + \frac{\omega}{2} \sum_{\alpha} (p_{\alpha}^2 + q_{\alpha}^2), \quad (41)$$

where only one vibration of the type F_2 with coordinates q_{α} ($\alpha = x, y, z$) is considered for simplicity, and V is the vibronic coupling parameter. The operators T_{α} in (41) act on the electronic wave functions ψ_x, ψ_y, ψ_z , with

$$\langle x | T_z | y \rangle = \langle y | T_z | x \rangle = \langle x | T_y | z \rangle = \langle z | T_y | x \rangle = \langle y | T_x | z \rangle = \langle z | T_x | y \rangle = 1, \quad (42)$$

while the remaining matrix elements of the operators T_{α} are equal to zero. Since the operators T_{α} are non-commuting, it is impossible to diagonalize the linear term in (41) for all q_{α} . We consider therefore two limiting cases: 1) $V \ll \omega$ (weak binding) and 2) $V \gg \omega$ (tight binding).

a) In the case of weak binding we can regard the linear term in (41) as a perturbation and carry out on \mathcal{H} a contact transformation of the type (14) with a generator

$$S = -\frac{V}{\omega} \sum_{\alpha} p_{\alpha} T_{\alpha}, \quad (43)$$

which eliminates from \mathcal{H} the linear term and relegates its contribution to the second order:

$$\begin{aligned} \mathcal{H}' = \mathcal{H} + \frac{i}{2} [S, \mathcal{H}] = \mathcal{H}_0 - \frac{V^2}{\omega} - \frac{i}{2} \frac{V^2}{\omega} \{ [T_x, T_y] (p_x q_y - q_x p_y) \\ + [T_x, T_z] (p_x q_z - q_x p_z) + [T_y, T_z] (p_y q_z - q_y p_z) \} \\ = \mathcal{H}_0 - \frac{V^2}{\omega} + \frac{V^2}{2\omega} (\Pi \Lambda), \end{aligned} \quad (44)$$

where $\Pi = \mathbf{q} \times \mathbf{p}$ is the vibrational angular momentum, while $-\Lambda = [\mathbf{T} \times \mathbf{T}]$. Just like \mathcal{H} , the Hamiltonian \mathcal{H}' has spherical symmetry. For the dipole moment we obtain from (15), taking (43) into account,

$$\mu_{\alpha} = -\frac{V}{\omega} \frac{\partial \mu}{\partial q_{\alpha}} T_{\alpha}. \quad (45)$$

For real molecules, a typical value is $\partial \mu / \partial q \sim 0.1 \text{ D}$, and if $(V/\omega) \sim 0.1$, then the Jahn-Teller and anharmonic dipole moments (Chap. 4) (as well as the centrifugal in

the case of large J ; Chap. 3) can have the same order of magnitude, and since the selection rules with respect to the quantum numbers are the same for the Jahn-Teller transitions as for the anharmonic transitions, the identification of the transition can encounter certain difficulties.

b) In the case of tight binding, the molecule can become stabilized in one of four equivalent configurations.^[54] Then the potential-energy surface is a cubic hypersurface whose equipotentials are determined by the constant values $q_x^2 + q_y^2 + q_z^2$ and $q_x q_y q_z$, while the positions of the maxima are determined from the conditions $|q_x| = |q_y| = |q_z|$ and $q_x q_y q_z = -\Delta^3$, where $\Delta = 2V/3\omega$.^[54-56] In each of these minima, the geometric configuration (and the electron-density distribution) of the molecule has symmetry (C_{3v}), i. e., one of the A-B bonds is longer (or shorter) than the remaining three equivalent bonds. If the barriers between the minima is much higher than the vibration energy (static Jahn-Teller effect), then the molecule executes small vibrations near equilibrium in one of the minima, and has a constant dipole moment that depends on the distribution of the electron density of the molecule at the minimum. Owing to the presence of four minima, the vibronic functions turn out to be quadruply degenerate. This degeneracy, however, is fortuitous and is lifted when account is taken of the off-diagonal elements of the quadratic term and of terms of higher order in (41).^[58] As a result, the quadruply degenerate level splits into a triply degenerate level and a nondegenerate level, of the type $F_2 + A_1$ in the case of triplet F_2 and $F_1 + A_2$ in the case F_1 . If the wave functions ψ_i ($i=1, 2, 3, 4$) of different minima overlap weakly, the splitting is given by^[58]

$$\Delta(A-F) = \frac{16}{9} E_{JT} \exp\left(-\frac{4E_{JT}}{3\omega}\right), \quad (46)$$

where $E_{JT} = 2V^2/3\omega$. The wave functions of the A and F levels are linear combinations of ψ_i ^[55]:

$$\left. \begin{aligned} \psi_A &= \frac{1}{2}(\psi_1 + \psi_2 + \psi_3 + \psi_4), \\ \psi_E &= \frac{1}{2}(\psi_1 - \psi_2 + \psi_3 - \psi_4), \\ \psi_T &= \frac{1}{2}(\psi_1 - \psi_2 - \psi_3 + \psi_4), \\ \psi_C &= \frac{1}{2}(\psi_1 + \psi_2 - \psi_3 - \psi_4), \end{aligned} \right\} \quad (47)$$

where no account is taken of the factors due to the non-orthogonality of ψ_i which are close to unity in the case of a small overlap of ψ_i . The nonzero dipole-moment matrix elements are then^[58]

$$\langle \xi | \mu_z | \eta \rangle = \langle \xi | \mu_x | \zeta \rangle = \langle \eta | \mu_z | \zeta \rangle = (\langle \psi_1 | \mu_z | \psi_1 \rangle - \langle \psi_1 | \mu_z | \psi_2 \rangle), \quad (48)$$

where $\langle \psi_1 | \mu_z | \psi_1 \rangle$ is the constant dipole moment of the molecule in one of the minima, while the second term is close to zero at large V . Unfortunately, it is impossible to present a reliable estimate of the dipole moment in this case. However, if the difference between the bond lengths of the non-equivalent bonds is $\sim 0.1 \text{ \AA}$, then the dipole moment can be $\sim 0.1 \text{ D}$, i. e., larger by one or two orders than the anharmonic dipole moment. It appears that this is the situation in the ground vibronic

state of the ion CH_4^+ .^[60]

Klemperer and co-workers^[61] have recently performed an experiment on the focusing of the molecules CF_4 , CCl_4 , SiF_4 , SiCl_4 , GeCl_4 , and TiF_4 , TiCl_4 , VF_4 , VCl_4 in a quadrupole electrostatic field for the purpose of elucidating the polar properties of these molecules. The second group of molecules (TiF_4 etc.) is of interest from the point of view of the Jahn-Teller effect, for according to the results of quantum-mechanical calculations the ground vibronic state of these molecules can be of the 2F_2 type, wherein the molecules can have a Jahn-Teller dipole moment. They have shown^[61] that all the investigated molecules have a small dipole moment (less than 0.01 D) and the isotopic effect^[61b] was used to ascertain the anharmonic nature of the polarity of the molecules of the first group (CF_4 etc.). The nature of the polarity of the second group has not been ascertained, however.

Summing up this chapter, we must stress that the Jahn-Teller dipole moment in the degenerate electronic state can be of the same order (and larger) than the anharmonic dipole moment. Unfortunately, however, the electronic ground state of an overwhelming majority of nonpolar moment is nondegenerate. To observe Jahn-Teller effects in excited degenerate states, methods of double optical and microwave therefore become particularly vital.^[62, 63]

6. CONCLUSION

The foregoing brief review demonstrates the importance of research on weak rotational transitions. Results of an investigation of forbidden rotational spectra provide unique information on the structure and on the electro-optical properties of molecules. In particular, symmetrical-top transition frequencies are used to determine the values of the rotational constants $A(C)$, D_K , and others, which cannot be determined from allowed transitions. From the transition intensities we can determine the relative signs of the electro-optical parameters.^[64]

The results of laboratory investigation of radiative (as well as collision-induced) transitions make it possible to ascertain the mechanism of the formation and relaxation of excited molecules in the interstellar medium.^[65-67] It has been shown, in particular, the forbidden radiative transitions, despite their large lifetimes, are capable of competing with collision transitions in the establishment of equilibrium between rotational levels of interstellar ammonia. In addition, the question of which rotational levels can be metastable or strictly stable can be answered only if rigorous selection rules are established. For example, ammonia levels with $J=K$ are metastable with respect to dipole transitions with $\Delta K=0$, but when the centrifugal and collision transitions are taken into account it becomes clear that all levels except the levels with $J, K=0, 0$ and $1, 1$ have a finite albeit long lifetime, 40 years for the radiative transition $3, 3-2, 0$, 200 years for $2, 2-1, 1$, etc.^[65-67] It becomes also possible^[68] to observe centrifugal transitions of methane in the spectra of the atmospheres of Jupiter, Saturn, Uranus, Neptune, and Titan (satellite

of Saturn), in which methane is one of the principal components.

From the theoretical point of view, the best understood are the centrifugal mechanism for the ground vibronic state (Chap. 3) and the anharmonic mechanism for isolated vibrational states (Chap. 4). The role of random resonances of the Fermi and Coriolis type in these spectra is not clear. As shown in Chap. 5, the Jahn-Teller transitions admit of an approximate theoretical analysis only within the limits of vibronic weak and tight binding, although it is intuitively clear that in intermediate states the value of the dipole moment should also be intermediate, although there are still no reliable estimates of the dipole moment.

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